

**CHARACTERIZING NANOPHASE MATERIALS ON MARS: SPECTROSCOPIC STUDIES OF ALLOPHANE AND IMOGOLITE.** T.J. Jeute<sup>1</sup>, L.L. Baker<sup>1</sup>, Z. Abidin<sup>2</sup>, J.L. Bishop<sup>3</sup>, and E.B. Rampe<sup>4</sup>, <sup>1</sup>Department of Geological Sciences, University of Idaho (Moscow, ID), <sup>2</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Bogor Agricultural University, Indonesia, <sup>3</sup>SETI Institute & NASA Ames (Mountain View, CA), <sup>4</sup>Jacobs-JETS at NASA-JSC (Houston, TX).

**Introduction:** Identification of allophane and other highly variable amorphous and nanophase mineral materials has provided clues about the aqueous geochemical environment of Mars [1,2]. These materials likely represent partially altered or leached basaltic ash [3] and therefore, could represent a geologic marker for where water was present on the Martian surface. Further, they may indicate regions of climate change, where surface-water was not present long enough to form clays [1]. Characterization of these materials is important for increasing spectral recognition capacities of our current Martian science array.

**Geologic Context:** Allophane is an amorphous or poorly crystalline hydrous aluminosilicate material [3,4,5]. On Earth, allophane is typically associated with volcanic ash or fine-grained pumice bearing soils and forms under neutral to mildly acidic pH regimes (5-7) [e.g. 3,4,5]. Allophane has been identified in clay-bearing regions on Mars using thermal emission spectroscopy (TES) [2]. Additionally, MSL Curiosity instruments have identified an amorphous phase in soils that may contain allophane [6]. This evidence suggests allophane may be a common component of clay-bearing regions of Mars [2].

**Methods:** We created a suite of nanophase mineral materials of varying compositions. These synthetic samples were then spectrally characterized using Fourier transformed IR (FTIR) spectroscopy, visible/near-infrared (VNIR) reflectance spectroscopy, thermal infrared emission spectroscopy (TIR) and a field emission scanning electron microscope (FESEM). Verification of compositions will be carried out by supernatant analysis on an inductively-coupled plasma atomic emission spectrometer (ICP-AES). Compositions of the nanophase materials range from high-Si allophane (molar Al:Si = 1:2) to protoimogolite (molar Al:Si = 2:1), while spanning a range of Fe<sup>3+</sup> isomorphically substituted for Al from 0-10 mol%. These compositions span the range observed in natural terrestrial allophanes [4].

**Allophane Synthesis Procedures.** Synthetic allophane samples were created using an established method that has been modified to produce allophane with Fe isomorphically substituted for Al in octahedral coordination [7,8]. In this method, NaOH is titrated slowly into a mixture of 0.1 M AlCl<sub>3</sub> and FeCl<sub>3</sub> and tetraethyl orthosilicate (TEOS) under vigorous stirring to precipitate a gel. The gel is aged at 95 °C for five days

before being separated by centrifugation, purified by dialysis against flowing deionized water, and freeze-dried for further analysis.

**Imogolite Synthesis Procedures.** Synthetic imogolite samples were created by Z. Abidin using a previously established method [9]. Aliquots of AlCl<sub>3</sub> solution were simultaneously mixed with orthosilicic acid to yield an Al:Si ratio of 2:1. The solution mixtures were titrated with NaOH at a rate of about 0.5 mL NaOH min<sup>-1</sup> to an OH:Al molar ratio of 2. The Si concentration of the resulting solution was 1.6 mM. Supernatant solutions had pH values from 3.98 to 4.03. The solution mixtures were heated in an autoclave at 110°C for 48 hours. After the collected precipitates were flocculated by NaCl, the sample was dialyzed using cellulose tubes against distilled water until they were free of sodium and chloride ions, then freeze-dried.

**FESEM Analysis.** Synthetic allophane and imogolite samples were characterized using a Zeiss Supra 35 Variable-Pressure FEG SEM. Samples were mounted on carbon tape and analyzed at an accelerating voltage of 5kV. Semi-quantitative elemental analysis was carried out at 15kV using a Noran System Six EDS. An FESEM view of an imogolite is shown in Figure 1 and of an allophane is shown in Figure 2.

**FT-IR.** IR characterization was performed on a Perkin-Elmer Spectrum System 2000 FT-IR spectrometer. Samples were diluted to ~3 wt.% sample with optical KBr and measured as loose powder using a Perkin-Elmer diffuse reflectance accessory. Kubelka-Munk transformed spectra are shown in Figure 3 and resemble typical spectra of natural and synthetic allophanes.

**ICP-AES.** Verification of synthesis product was performed by analysis of supernatant solution. Supernatant analysis was performed using a ThermoFisher iCAP Duo inductively-coupled plasma atomic emission spectrometer (ICP-AES).

**Emission spectroscopy.** Thermal Infrared (TIR) emissivity spectra will be collected from 5-50 μm at the Mars Space Flight Facility at Arizona State University as in past studies [2,10]. Samples will be pressed into pellets and heated to 80 °C to increase the signal-to-noise ratio.

**Reflectance spectroscopy.** Reflectance spectra of undiluted, particulate samples were measured at the SETI Institute from 0.35 to 2.5 μm using an ASD spectrometer and will be measured at RELAB, Brown Uni-

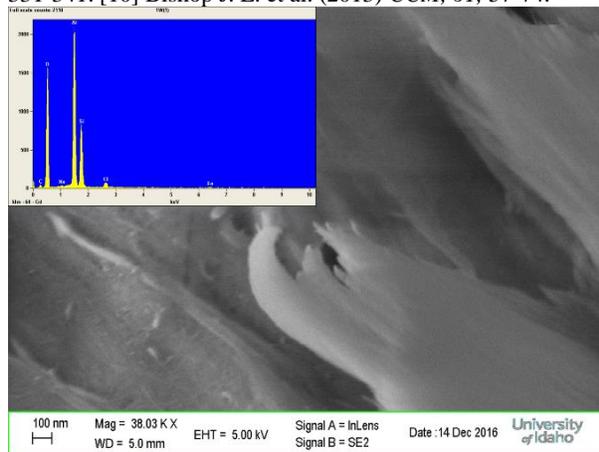
versity as in past studies [10]. FTIR spectra are measured from 1-50  $\mu\text{m}$  relative to a rough gold surface and are scaled near 1.2  $\mu\text{m}$  to bidirectional spectra measured from 0.3 to 2.5  $\mu\text{m}$  relative to halon. VNIR spectra are shown in Figure 4.

**Discussion:** Previous synthetic work suggested that the amount of Fe that can substitute in synthetic allophane varies with Si content [8]. Current synthetic work suggests otherwise in that we have achieved 10 mol.% Fe isomorphically substituted for Al in allophanes with Al:Si compositions of 1:1. This substitution, and the structural position of Fe in the synthetic imogolite samples, will be confirmed using Fe K-edge X-ray absorption spectroscopy.

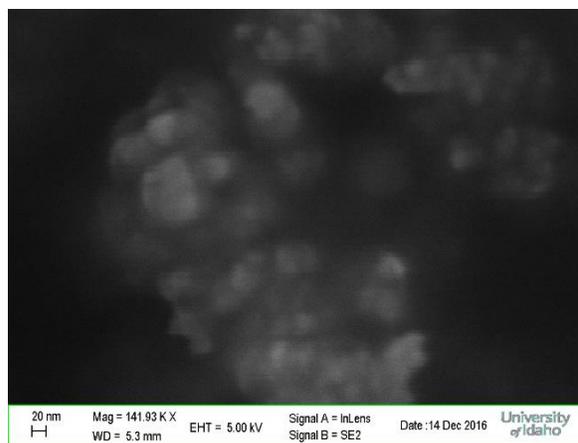
**Future Work:** Currently, all Fe-enriched allophanes have incorporated  $\text{Fe}^{3+}$ ; however, under Martian conditions  $\text{Fe}^{2+}$  may be a cation of interest. Therefore  $\text{Fe}^{2+}$ -enriched allophanes will be synthesized from de-aerated solutions under an argon atmosphere.

The presence of high Si in various regions of Mars indicates that an amorphous Si species such as opaline silica may be of importance. Opaline silica with varying amounts of Fe incorporated will be synthesized as well for spectral characterization.

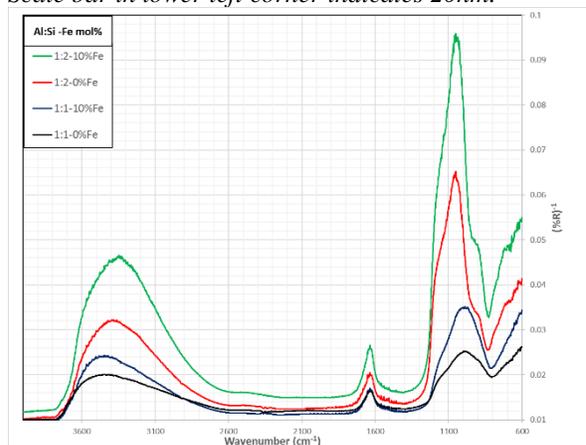
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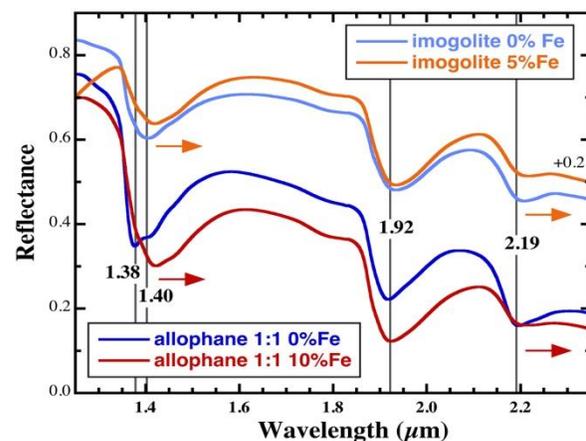
**Figure 1.** FESEM image of synthetic imogolite samples with inset EDS analysis. Peaks shown from left to right are O, Al, Si, Cl and Fe.



**Figure 2.** FESEM image of synthetic allophane sample. Scale bar in lower left corner indicates 20nm.



**Figure 3.** Kubelka-Munk transformed FT-IR data for selected allophane samples.



**Figure 4.** VNIR reflectance spectra of selected allophane and imogolite samples. Gray lines mark allophane bands. Shifts towards longer wavelengths were observed with the addition of Fe for OH bands near 1.4 and 2.2  $\mu\text{m}$ .

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